

# FABRICATION OF MIXED MATRIC MEMBRANE INCORPORATED WITH MODIFIED SILICA NANOPARTICLES FOR BISPHENOL A REMOVAL

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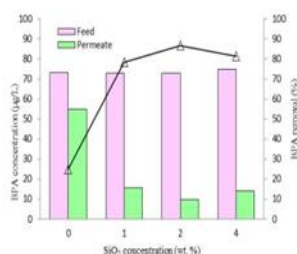
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## Graphical abstract



## Abstract

The introduction of inorganic nanoparticles in polymeric dope solution for the fabrication process of membrane can potentially enhance the separation performances of membrane without negatively affecting its permeability. In this study, hollow fiber mixed matrix membranes were prepared by incorporating polyethersulfone (PES) membranes with silicon dioxide (SiO<sub>2</sub>) nanoparticles at different concentration. Prior to separation tests, the prepared membranes were characterized by SEM, EDX, DSC, water contact angle, and FTIR-ATR in order to study the impact of silica nanoparticles on the properties of the membranes. Bisphenol A (BPA) was selected as the subject compound of this study because it is one of the emerging pollutants that have been frequently detected in the water treatment plant (WTP). BPA was spike into the pre-treated water sample taken from the WTP and was used as the feed solution to evaluate the membrane performance in terms of water flux and removal rate. The addition of SiO<sub>2</sub> was reported to improve the hydrophilicity of membrane and induce greater micro-voids formation in the membrane structures, leading to increased water flux during BPA filtration process. The presence of more silanol (Si-OH) and siloxane (Si-O-Si) bonding groups resulted from increased SiO<sub>2</sub> contents in membrane has improved membrane adsorption rate and further increased BPA removal.

**Keywords:** Mixed matrix membranes; polyethersulfone; silicon dioxide; bisphenol A; adsorption, water treatment plant

## Abstrak

Pengenalan nanopartikel bukan organik dalam larutan polimer dadah untuk proses fabrikasi membran berpotensi meningkatkan prestasi pemisahan membran tanpa memberi kesan negatif kepada kebolehtelapan. Dalam kajian ini, gentian berongga bercampur membran matriks telah disediakan dengan menggabungkan polyethersulfone (PES) membran dengan silikon dioksida (SiO<sub>2</sub>) nanopartikel pada kepekatan yang berbeza. Sebelum ujian perpisahan, membran tersedia telah ditentukan oleh SEM, EDX, DSC, sudut sentuhan air, dan FTIR-ATR bagi mengkaji kesan nanopartikel silika pada sifat-sifat membran. Bisphenol A (BPA) telah dipilih sebagai subjek kajian kerana ia adalah salah satu pencemaran yang baru muncul yang telah kerap dikesan di loji rawatan air (LPA). BPA telah dimasukkan ke dalam sampel pra-rawatan air yang diambil dari LPA dan telah digunakan sebagai penyelesaian untuk menilai prestasi membran dari segi fluks dan kadar penyingkiran air. Penambahan SiO<sub>2</sub> seperti yang dilaporkan meningkatkan hidrofilik membran dan mendorong pembentukan lebih besar mikrolompang dalam struktur membran, yang membawa kepada peningkatan fluks air semasa

proses penapisan BPA. Kehadiran lebih kumpulan ikatan silanol (Si-OH) dan siloksan (Si-O-Si) ini adalah hasil daripada peningkatan kandungan SiO<sub>2</sub> dalam membran yang telah menambah baik kadar penjerapan membran dan meningkatkan lagi penyingkiran BPA.

*Kata kunci:* Membran bercampur matriks, polyethersulfone, silicon dioxide, bisphenol A, penjerapan, loji rawatan air

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## 1.0 INTRODUCTION

Bisphenol A (BPA) is one of the emerging pollutants that have been frequently detected in the nation's water supplies, but it is often present at lower concentrations that are not exceeding the tolerable daily intake [1]. Even though these compounds are less persistent in the environment, their continuous introduction might lead to adverse effects [2]. This is because BPA is an endocrine disruptor compounds (EDCs) that can interrupt the endocrine system by mimicking, blocking or disrupting functions of hormones in living organisms [3].

The conventional water treatment plant (WTP) is generally designed to remove the majority of chemical and microbial contaminants, but its efficiency of BPA removal is found to be poor as reported in literature [4-7]. Studies regarding the removal of BPA during water treatment have been limited due to the low extremely concentration of this compound ( $\mu\text{g/L}$  to  $\text{ng/L}$  level) in water sources, making sample analysis very difficult [8]. Apart from that, the demand for better water quality has led to more stringent regulations. At the moment, BPA is not listed yet as regulated contaminant in drinking water standards and its risks related to drinking water consumption have yet to be fully assessed. Little is known about the chronic effects of daily exposed to low level of BPA in drinking water [5]. In view of this, more research is needed for a new water purification process that can effectively eliminate the BPA from water sources.

It was found that the membrane separation process is suitable for drinking water treatment as the process does not utilize any chemicals [9]. Membranes have been generally considered as a replacement for many unit processes in WTP such as sand filtration, carbon adsorption and ion exchange [10]. This is due to their many advantages that relate to the water quality and less footprint compared to the conventional processes [11]. Intensive efforts have been made to determine the ability of the membrane in BPA removal [3, 8, 12-15]. Ultrafiltration (UF) membrane is one of the membrane processes that have great potential in the treatment of drinking water supplies owing to its low cost and high efficiency [9]. A study has revealed that UF membrane is capable of removing 92% of BPA spike in the concentration ranging from 100 to 600  $\mu\text{g/L}$  and was reported that adsorption is the major mechanism for removal of BPA [13].

The selection of materials used in membrane making is crucial in determining the effectiveness of UF membranes in removing the target compound. Polymeric membranes are commonly employed for water treatment as they produce good physicochemical properties [16]. Polyethersulfone (PES) is commonly used polymeric material for the fabrication of UF membrane because it can provide high mechanical, thermal (up to 75°C) and chemical resistances. Furthermore, PES demonstrates reasonable pH tolerances (ranging from 4 to 10), good chlorine resistance, and high flexibility that are needed for a UF membrane [17, 18]. Nevertheless, PES-based membrane has a major drawback of hydrophobicity. Its relatively high hydrophobic nature has made it prone to fouling problems [19]. In order to overcome the problem, a variety of organic or inorganic additives was utilized to increase the hydrophilicity of the PES membrane.

The addition of nanoparticles to the polymeric matrix has shown the potential to improve its hydrophilicity, selectivity and mechanical strength [19-21]. For drinking water application, silica nanoparticles are preferable to be incorporated into membrane because silica exhibits lower toxicity compared to other nanoparticles and is also environmentally inert [20]. The main objective of this study was to prepare PES-SiO<sub>2</sub> mixed matrix membranes made of different concentration of modified SiO<sub>2</sub> via phase inversion technique in order to evaluate the flux and removal performance of BPA. The membranes were characterized with respect to their physical morphology and chemical properties using several analytical instruments.

## 2.0 EXPERIMENTAL

### 2.1 Materials

Polyethersulfone (PES) polymer was purchased from Arkema Inc. (USA). Silicon dioxide (SiO<sub>2</sub>) nanoparticles with average particle size of 10-20 nm were used as inorganic additives. Sodium dodecyl sulfate (SDS) was used to modify SiO<sub>2</sub> nanoparticles by reducing their agglomeration tendency. Polyvinylpyrrolidone (PVP-40 kDa) was used as pore former agent while N,N-dimethylacetamide (DMAc) as solvent. BPA (purity >97%) was used as target compound in filtration experiment. All of these chemicals were supplied by Sigma Aldrich (USA). For HPLC analysis, the solvent

used for mobile phase was acetonitrile supplied by Merck (USA)

## 2.2 Membrane Preparation

Firstly, the  $\text{SiO}_2$  nanoparticles were modified using SDS solution according to the work of [22]. Next, a pre-weighed DMAc solvent was added with 18 wt.% PES pellets. Then the solution was stirred at 600 rpm until all the PES pellets were completely dissolved and homogenized. After that, 6 wt.% PVP and  $\text{SiO}_2$  nanoparticles of various loading (0, 1, 2 or 4 wt.%) were added to produce dope solutions of different properties. The dope solution was then ultrasonic-vibrated for 30 min to remove air bubbles from the solution and to ensure good dispersion of the particles prior to spinning process. The PES- $\text{SiO}_2$  composite membranes were prepared by phase inversions method. The hollow fiber membranes were spun by dry/wet spinning method with an air gap of 10 cm. The non-solvent (bore fluid) used was deionized water while external coagulation bath was tap water at  $25 \pm 1^\circ\text{C}$ . A spinneret with 1.25/0.55 mm orifice outer/inner diameter was used for the spinning of the dope solution where the dope extrusion rate was controlled at 3 mL/min while the bore fluid rate at 1.8 mL/min. The solidified hollow fiber membranes in the coagulation bath that emerged from the spinneret was guided through two water baths before being collected by a wind-up drum. The spun hollow fibers were stored in the water bath for 24 h to remove any residual of DMAc and PVP additives. Later, post treatment of membranes were carried out using 10 vol.% of glycerol in water for another 24 h to reduce fiber shrinkage and pore collapse during air-drying.

## 2.3 Water Sampling and Preparation of BPA Stock Solution

The water sample was taken from Water Treatment Plant (WTP) of Sungai Skudai, Johor Bahru, Malaysia as shown in Figure 1. The sample was specifically collected from the filter water tank whereby the surface water has undergone pre-treatment process. For this study, the water sample was spiked with BPA concentration of 100  $\mu\text{g/L}$  as feed solution for the UF system. The working standard solutions for BPA was prepared in the range of 100 to 20  $\mu\text{g/L}$  by diluting BPA stock solution of 100 mg/L in HPLC grade water to obtain the calibration standard.



**Figure 1** Location of water treatment plant of Sungai Skudai, Johor Bahru (Coordinate:  $1^\circ 33' 20.6''\text{N}$ ,  $103^\circ 39' 49.4''\text{E}$ )

## 2.4 Membrane Characterization

### 2.4.1 Contact Angle Measurement

The hydrophilicity of the membranes was measured using a contact angle system (Dataphysics, OCA 15Pro) where the measurement was made by the angle between the membrane surface and the meniscus formed by the water. The average of at least 5 measurements was reported.

### 2.4.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) Analysis

The morphology of the membrane was characterized by Tabletop SEM (TM300, Hitachi). The membrane samples were immersed in liquid nitrogen, and then fractured. The cross-section and surface of membrane samples were sputtered with platinum before transferred to the microscope to be examined. The quality of dispersion and also the existence of  $\text{SiO}_2$  on the membrane surface were examined by EDX (QUANTAX 70, Bruker).

### 2.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The surface functionalization of  $\text{SiO}_2$  nanoparticles with membrane was analysed using Fourier transform infrared spectroscopy (FTIR, NICOLET 5700 FT-IR, Thermo Electron Corporation) recorded in the range of  $800\text{--}1800\text{ cm}^{-1}$  by the attenuated total reflection (ATR) technique.

### 2.4.4 Differential Scanning Calorimeter (DSC) Analysis

The thermal stability of the membranes was determined using differential scanning calorimeter (DSC822<sup>e</sup>, Mettler Toledo). The effect of  $\text{SiO}_2$  nanoparticles on glass transition temperature ( $T_g$ ) of

membrane was observed at the heating rate of 10°C min<sup>-1</sup> up to 300°C.

### 2.5 Flux and BPA Removal Experiments

The membrane performance was evaluated with respect to flux and BPA removal using a cross-flow permeation system. Membrane samples were compacted at 300 kPa with distilled water for 1 h before any measurements were taken. The water flux of each membrane was then measured at 100 kPa by determining the volume of permeate collected at time interval of 10 min by the following equation:

$$J_w = V/At \quad (1)$$

where  $J_w$  is the water flux (L/m<sup>2</sup> h),  $V$  is the permeate volume (l),  $A$  is the membrane area (m<sup>2</sup>) and  $t$  is the time (h).

BPA removal was measured at 100 kPa using the same system by spiking 100 µg BPA in 1 L water sample. The BPA concentration in the feed and permeate samples were determined by ultra-high performance liquid chromatography (UHPLC) system (Agilent Technologies, USA) using a column ZORBAX Eclipse Plus C18, 1.8 µm (2.1 × 100 mm) (Agilent, USA). The excitation and emission of Fluorescence detector were set at 225 nm and 310 nm, respectively. While for UV detector was set at a wavelength of 230. The mobile phase was pumped under isocratic conditions at flow rate of 1 mL/min consisting of (40:60, v/v) acetonitrile:water. The column temperature was set at 40°C with sample injection volume of 20 µL. BPA removal ( $R$ ) by membranes was calculated by the following equation:

$$R (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where  $C_p$  is the concentration of permeate (µg/L) and  $C_f$  is the concentration of feed (µg/L)

## 3.0 RESULTS AND DISCUSSION

### 3.1 Full Hardware Setup

#### 3.1.1 Calibration Curve, Limit of Detection and Quantification

Calibration curve was plotted to estimate the concentration of BPA in the feed tank and permeate based on linear regression of BPA concentrations versus detector responses at five concentration levels (20–100 µg/L) as shown in Figure 2. The correlation coefficient display the peak height to concentration of more than 0.9 and the obtained detection limit was 15 µg/L while the quantification limit was 50 µg/L.

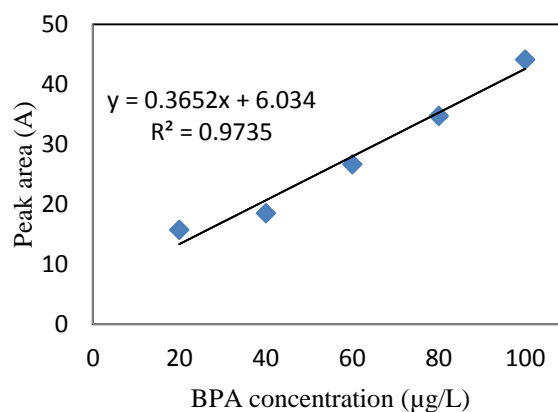


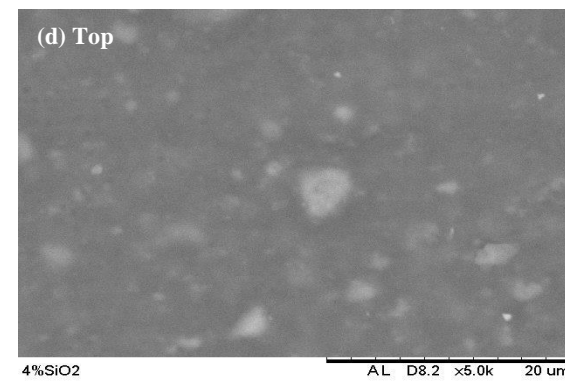
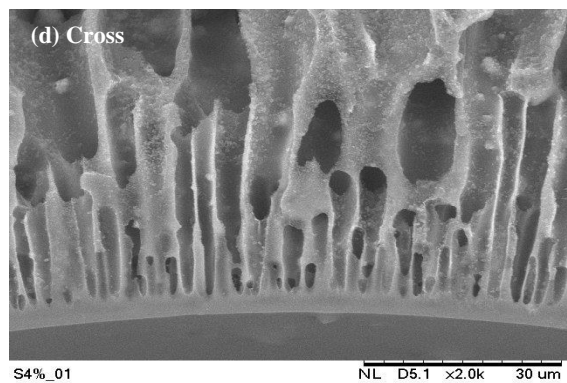
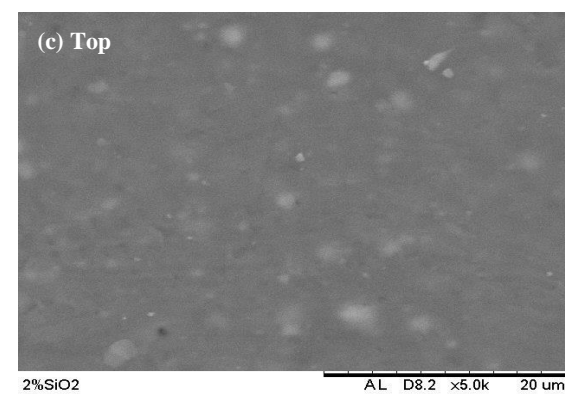
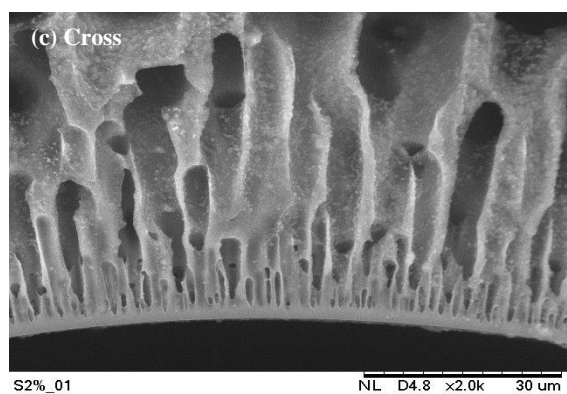
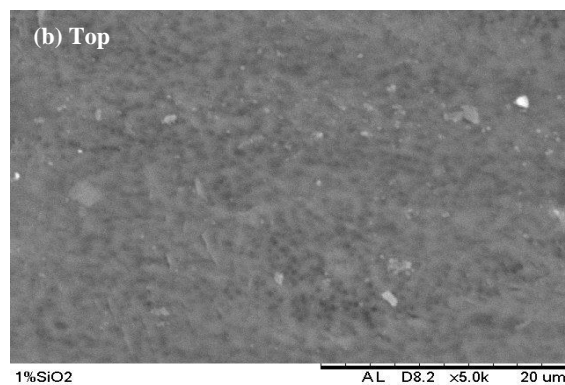
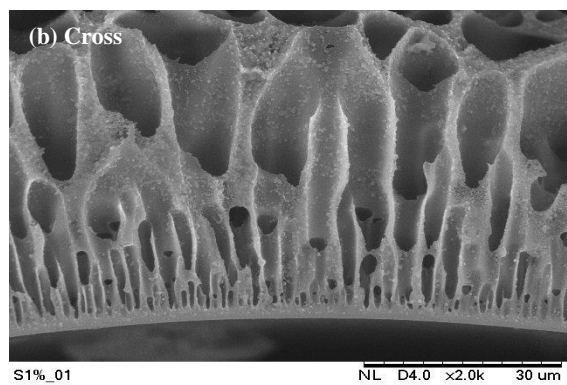
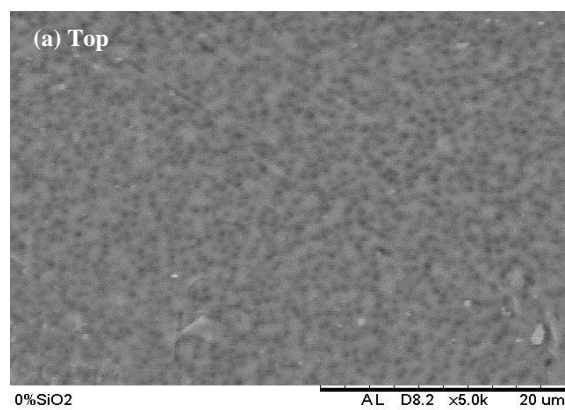
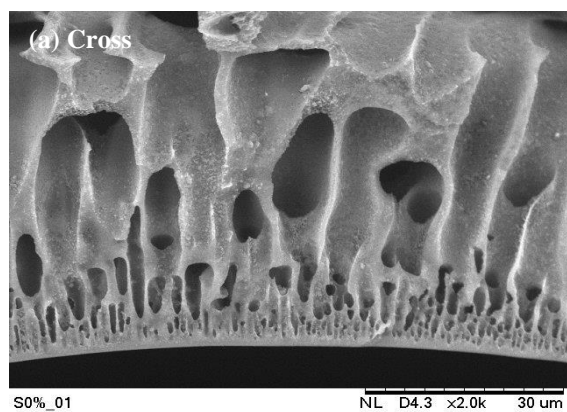
Figure 2 Calibration plots for BPA standard

### 3.2 Membrane Morphology

The morphologies of the membrane surface and cross section were observed with SEM and the results are shown in Figure 3. The characteristic morphology of the membranes consists of dense sub-layer with finger-like structures and fully developed macro-voids. The addition of SiO<sub>2</sub> had increased the finger-like structure and the connectivity of the pores between the sub-layer in comparison to the control PES membrane. Figure 3 also shows that the addition of SiO<sub>2</sub> tended to induce the macro-voids formation in the membrane where the cross section structure became more porous. The enlarged macro-void structure occurred due to the fast exchange of solvent and non-solvent in the phase inversion process [23]. On contrary, the formation of micro-voids is suppressed at high concentration of SiO<sub>2</sub> nanoparticles (4 wt.%) and more compact and denser structures were formed as evidenced in Figure 3(d). This is because the addition of SiO<sub>2</sub> in the polymer solution would increase the dope viscosity and delay the exchange rate of solvent and non-solvent in the phase inversion process. As a result, a less porous membrane structure was produced [17].

The top surface of membranes showed the existence of SiO<sub>2</sub> on the external surface of each membrane. The white color spotted over the membrane surface indicates the location of the SiO<sub>2</sub> nanoparticles. It can be seen that SiO<sub>2</sub> nanoparticles were dispersed across the surface of PES-SiO<sub>2</sub> membranes. The distribution of SiO<sub>2</sub> was almost uniform, indicating their compatibility with polymeric membrane. The highest content of silica was observed in 4 wt.% SiO<sub>2</sub> membrane followed by 2 wt.% and 1 wt.% SiO<sub>2</sub> membrane. However, these nanoparticles tended to agglomerate easily at highest content of SiO<sub>2</sub> used.

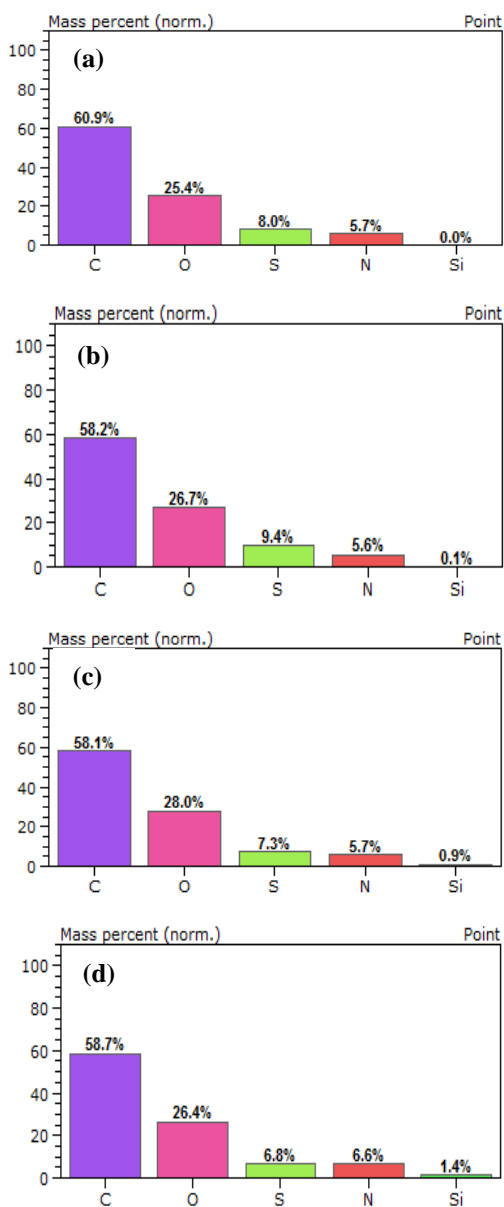




**Figure 3** Cross-section (magnification =  $\times 2000$ ) morphologies and top surface (magnification =  $\times 5000$ ) of the PES-SiO<sub>2</sub> mixed matrix membranes with (a) 0, (b) 1, (c) 2 and (d) 4 wt.% SiO<sub>2</sub>

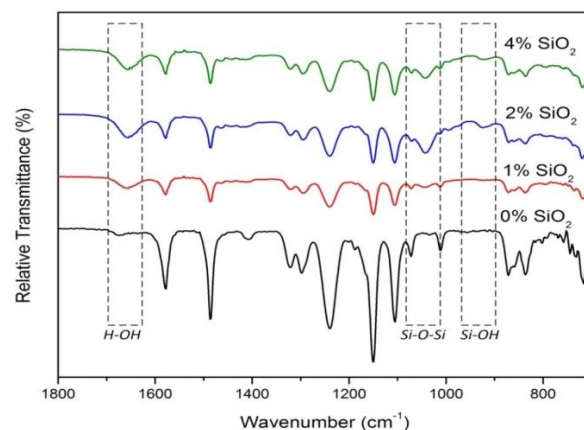
### 3.3 EDX and FTIR Analysis

The elemental composition of membranes and their functional groups were investigated by EDX and FTIR analysis, respectively. The results of EDX analysis is shown in Figure 4. It was observed that the control PES membranes in Figure 4(a) only contained high amount of carbon, oxygen, sulfur, and nitrogen while in PES-SiO<sub>2</sub> membranes in Figure 4(b), (c) and (d), additional signal corresponded to silica was detected. The highest silica content (1.4%) was reported in PES membrane incorporated with 4 wt.% SiO<sub>2</sub> followed by membrane incorporated with 2 wt.% and 1 wt.% SiO<sub>2</sub> with 0.9% and 0.1% silica, respectively.



**Figure 4** EDX results of the surface of (a) control PES membrane and PES-SiO<sub>2</sub> membranes with (b) 1, (c) 2 and (d) 4 wt.% SiO<sub>2</sub>

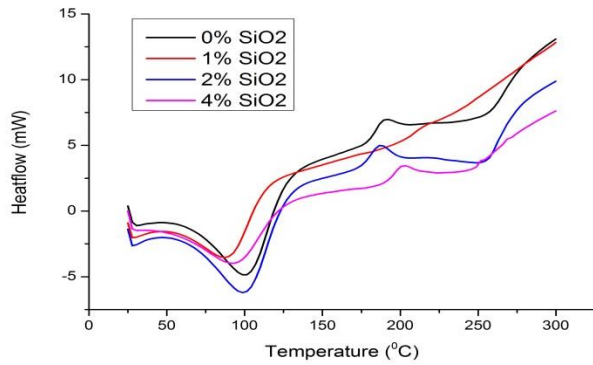
Figure 5 shows the FTIR spectra of the control PES and PES-SiO<sub>2</sub> membranes. The absorption band at 925 cm<sup>-1</sup> is attributed to Si-OH stretching. The broad H-O-H peaks observed at around 1656 cm<sup>-1</sup> is resulted from the existence of Si-OH or -OH groups while the absorption band at 1042 cm<sup>-1</sup> is the asymmetrical stretch vibration absorption of Si-O-Si [23]. The higher the amount of SiO<sub>2</sub> added, the greater the absorption band detected. These absorption peaks indicate that SiO<sub>2</sub> particles were successfully incorporated into the polymer matrices.



**Figure 5** FTIR spectra of control PES and PES-SiO<sub>2</sub> membranes

### 3.4 Thermal Properties of Membrane

Figure 6 shows the DSC results of the control PES and PES-SiO<sub>2</sub> membranes. Multiple glass transition temperatures ( $T_g$ ) were observed in the PES-SiO<sub>2</sub> mixed matrix membrane membranes whereby only single  $T_g$  was found in the control PES membrane. The occurrence of multiple  $T_g$  in mixed matrix membrane suggested the immiscibility of PES and SiO<sub>2</sub> nanoparticles in the polymeric solution. This is due to the amphiphilic structure of SDS compound that was used to modify SiO<sub>2</sub>, causing PES and SiO<sub>2</sub> nanoparticles not completely miscible during dope preparation. The PES membrane incorporated with 4 wt.% SiO<sub>2</sub> showed the highest  $T_g$  of 206.31°C followed by the membrane with 2 wt.% (196.73°C) and 1 wt.% (192.85°C) SiO<sub>2</sub>. The increase of  $T_g$  value with the addition of SiO<sub>2</sub> indicate improvement of thermal properties in membrane [24, 25].



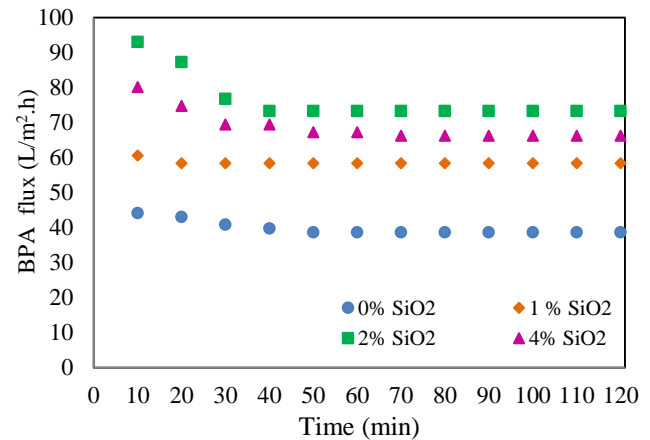
**Figure 6** DSC thermograms of control PES and PES-SiO<sub>2</sub> membranes

### 3.5 Flux and Removal Performance of BPA

The results of contact angles in Table 1 showed that the addition of SiO<sub>2</sub> nanoparticles in the PES matrices tended to decrease membrane contact angles from 77.9° to 71.0°. The lower the contact angle, the higher is the hydrophilicity of the membrane. These indicate that the addition of SiO<sub>2</sub> from 1 to 4 wt.% in the PES membrane has improved the hydrophilicity property of the membrane. As a result, higher water flux was achieved in the PES-SiO<sub>2</sub> membrane as shown in Figure 7. The highest BPA flux was found in the membrane incorporated with 2 wt.% SiO<sub>2</sub> (73.3 L/m<sup>2</sup>.h) while the lowest was by the control PES membrane (38.6 L/m<sup>2</sup>.h). This is because hydrophilic membranes have a strong tendency toward water that consequently hinder other molecules from adhering to the membrane surface [19] and increase the BPA flux in the PES-SiO<sub>2</sub> membranes. However, further increase in SiO<sub>2</sub> content from 2 to 4 wt.% has negatively affected water flux. This occurred as higher SiO<sub>2</sub> content tends to form highly viscous dope solution that delays membranes formation process. The movement of PES chains is compressed by formation of SiO<sub>2</sub> network, thus hindered the formation of macrovoid structure and reduced water permeability [26].

**Table 1** Contact angle of PES-SiO<sub>2</sub>

SiO <sub>2</sub> content (wt.%)	Contact angle (°)
0	77.9±0.3
1	74.9±0.5
2	73.9±0.3
4	71±0.4



**Figure 7** Flux decline behavior of control PES and PES-SiO<sub>2</sub> membranes according to the filtration time

Figure 8 shows the removal rate of BPA by control PES and PES-SiO<sub>2</sub> membranes. It can be seen that the removal rate was higher in the PES-SiO<sub>2</sub> membranes compared to the control PES membrane. The BPA removal was very high in the 2 wt.% SiO<sub>2</sub> membrane (87%) followed by 4 wt.% and 1 wt.% SiO<sub>2</sub> membrane with 82% and 79% recorded, respectively. While for the control PES membrane, the BPA removal was the lowest (25%). These indicate that the introduction of silica in the membrane matrices can give significant effect on BPA removal. This is because SiO<sub>2</sub> contain silanol groups that have high adsorption capacity for contaminants [27]. Thus, the addition of SiO<sub>2</sub> in the polymer matrixes will increase the silanol (Si-OH) and siloxane (Si-O-Si) bonding groups as shown in Figure 5, that act as adsorption sites for adsorbates at the membrane surface [28]. It is possible for BPA to interact with two or more silanol groups at a time and adsorb to the membrane surface [29]. Hence, the increase of SiO<sub>2</sub> in the polymer solution will increase the adsorption mechanism in the membrane and lead to better removal of BPA. In addition, the hydrophobic nature of BPA is also reported to be adsorbed easily toward membrane surface [30].



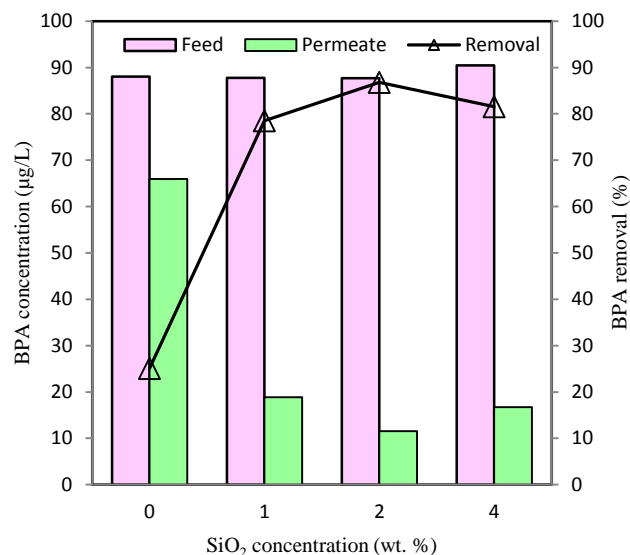


Figure 8 BPA removal of control PES and PES-SiO<sub>2</sub> membranes

## 4.0 CONCLUSION

PES membranes incorporated with different SiO<sub>2</sub> contents were fabricated in this work via phase inversion technique. Upon addition of SiO<sub>2</sub>, it was found that the cross-sectional morphology of membranes was altered with more macro-voids and finger-like structure detected. The EDX and FTIR analysis confirmed the successful incorporation of SiO<sub>2</sub> in the composite membranes owing to the silica element detected in EDX and the functional group of silicon bonding found in FTIR. The thermal properties of the membrane were improved with the addition of SiO<sub>2</sub> in the polymer solution. The membrane performance was investigated in terms of the BPA removal and flux behavior. The addition of SiO<sub>2</sub> in the PES membrane led to significantly higher water flux and BPA removal compared to the control PES membrane. The highest flux and removal of BPA was obtained in the membrane incorporated with 2 wt.% SiO<sub>2</sub>, achieving 73 L/m<sup>2</sup>.h and 85%, respectively. The increase of BPA removal is due to the increase of SiO<sub>2</sub> contents in the membrane which improves the adsorption for BPA.

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